A Continuum Theory That Couples Creep and Self-Diffusion

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In a single-component material, a chemical potential gradient or a wind force drives self-diffusion. If the self-diffusion flux has a divergence, the material deforms. We formulate a continuum theory to be consistent with this kinematic constraint. When the diffusion flux is divergence-free, the theory decouples into Stokes's theory for creep and Herring's theory for self-diffusion. A length emerges from the coupled theory to characterize the relative rate of self-diffusion and creep. For a flow in a film driven by a stress gradient, creep dominates in thick films, and self-diffusion dominates in thin films. Depending on the film thickness, either stress-driven creep or stress-driven diffusion prevails to counterbalance electromigration. The transition occurs when the film thickness is comparable to the characteristic length of the material. [DOI: 10.1115/1.1781176]

1 Introduction

Self-diffusion can generate stress in a single-component material. During deposition, for example, a thin film sometimes develops a compressive stress. One possible mechanism has to do with the injection of atoms into the film, [1]. Impinging atoms may not have enough time to find equilibrium positions on the film surface, and may diffuse into the film. Oxidation leads to analogous phenomena. For some materials, during oxidation, atoms may emit from the materials, causing tension in the materials, [2]. For other materials, notably silicon, atoms may inject into the materials, causing compression in the materials, [3]. Electromigration provides yet another compelling example. The conduction electrons motivate atoms to diffuse, generating tension upstream and compression downstream, [4].

The stress generated in the material depends on the deformation mechanism of the material. Only elastic property enters the consideration if inelastic deformation (i.e., creep) is either so slow as to be negligible, or so fast as to relax the stress field locally to a hydrostatic state. For electromigration along a thin line, encapsulated in a stiff dielectric, it was thought that local stress relaxes to a hydrostatic state long before diffusion along the line reaches a steady state, [5,6]. Experiments, however, have shown large deviatoric stresses, [7]. Indeed, the initial discovery of electromigration-induced stress was made in a wide aluminum film, which could only sustain in-plane stresses, [4].

This paper formulates a theory to couple self-diffusion and creep in single-component materials. The new theory will contain Stokes's creep and Herring's diffusion as special cases. Stokes's creep, as formulated in fluid mechanics, describes a velocity field and a pressure field; it neglects self-diffusion. Herring's theory, [8], for self-diffusion is in terms of the chemical potential, a scalar; it makes no attempt to equilibrate stress tensor field.

Our theory parallels that of nonreciprocal diffusion in multicomponent solid solutions (i.e., the Kirkendall effect) due to Darken [9] and Stephenson [10], and extends our previous one-dimensional theory, [11]. The theory rests on a kinematic constraint: the divergence in the self-diffusion flux must be accommodated by deformation. The remainder of this section recalls a few historic highlights of the mechanistic picture of creep and self-diffusion. Sections 2–4 describe the kinematics, energetics, and kinetics of the theory. Section 5 gives the coupled partial differential equations for the velocity field and the chemical potential field, and identifies the characteristic length in the theory. Sections 6 discusses examples of flows driven by stress gradient, wind force, and atomic injection or emission. Stress gradient-driven channel flow is dominated by creep in thick channels, and by self-diffusion in thin channels. Section 7 discusses an anisotropic rule to place diffusion flux divergence as strain rates in various directions.

That creep and self-diffusion in some materials result from the same atomistic process has been known for a long time. In a liquid, self-diffusion and creep are different macroscopic manifestations of the same microscopic fact: Molecules change neighbors readily in the liquid. Einstein [12] related the Brownian movement of a macroscopic particle in a liquid to the viscosity of the liquid. The Stokes-Einstein formula, derived by Einstein using Stokes's continuum solution, has since been applied to diffusion of molecules in liquids, including self-diffusion.

Nabarro [13] and Herring [8] related creep in a polycrystal to self-diffusion mediated by the motion of vacancies. By itself, the motion of vacancies does not change the crystal shape, but the creation and annihilation of vacancies at the grain boundaries do. Consequently, creep in the polycrystal is fast when the self-diffusivity is high and the grains are small. When the grain size approaches the molecular dimension, the Nabarro-Herring formula for polycrystals reduces to the Stokes-Einstein formula for liquids, except for a numerical factor. Similar comments apply to the Coble creep, [14], mediated by atoms diffusing on grain boundaries.

Needleman and Rice [15] formulated a theory for polycrystals, where atoms diffuse on grain boundaries and creep in grains. Here creep can result from the motion of dislocations. The two processes, self-diffusion and creep, occur in different places, but couple through a kinematic constraint. For two grains meeting at a grain boundary, the creep in the two grains accommodates the divergence of the diffusion flux on the grain boundary.

Our theory neglects the microstructure. Regardless of the specific microstructure, when a wind force motivates atoms to diffuse, the material must deform to accommodate the divergence of the self-diffusion flux. The main advantage of the theory is that simple and enlightening solutions may be obtained for coupled problems. The main drawback is that the theory may lead to wrong predictions at the size scale approaching or smaller than the microstructural feature size. The new theory can be applied, with virtues and vices of a continuum theory, to complex materials, and to crystalline materials when atoms also diffuse in grains, among other situations for which the Needleman-Rice theory is not in-

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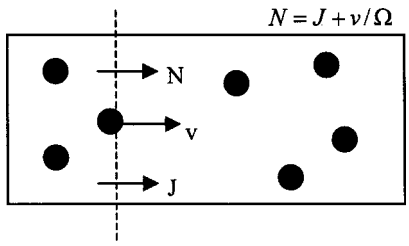

Fig. 1 The marker velocity *v* defines the convection flux, v/Ω. We can also independently measure the net atomic flux *N*. The atomic flux in excess of the convection flux defines the diffusion flux *J*.

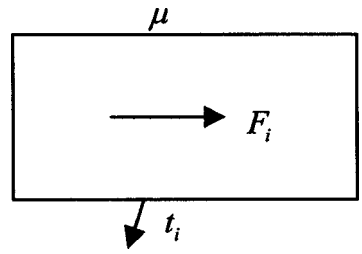

Fig. 2 The material is subject to three types of load: the wind force F_i in the volume, the traction t_i on the surface, and the chemical potential on the surface

tended. In particular, we will use the new theory to analyze electromigration-induced creep in Newtonian liquids.

2 Kinematics

When the two rate processes occur in separate places, creep in grains and diffusion on grain boundaries, there is no ambiguity about their distinct contributions to mass transport. When diffusion and creep occur in the same continuum space, how can their contributions be distinguished? We must give operational definitions of creep and self-diffusion without referring to the microstructure. Following Darken [9], we imagine that markers are dispersed throughout the material (Fig. 1). The markers in the material are analogous to leaves on a river. The flow of water carries the leaves, but is unaffected by their presence. The motion of the markers defines convection. The atomic flux in excess of convection defines diffusion. The markers should be small compared to the size scale in the flow of interest, but large compared to the atomic dimension so that the markers themselves diffuse negligibly.

We adopt the Eulerian approach. Let (x_1,x_2,x_3) be the coordinates of a fixed space. The field $v_i(x_1,x_2,x_3,t)$ is the velocity vector of the marker at position (x_1,x_2,x_3) at time t. Let Ω be the volume per atom in the body. Imagine a plane fixed in space and perpendicular to the axis x_i. The convection flux, v_i/Ω, is the number of atoms moving with the marker across the plane, per unit area per unit time. The net atomic flux, N_i, is the number of atoms across the plane, per unit area and per unit time. We can independently measure the marker velocity and the net atomic flux. The difference between the two fluxes defines the self-diffusion flux J_i, namely,

$$N_i = J_i + v_i/\Omega. \tag{1}$$

The net flux is the sum of the diffusion flux and the convection flux.

To demonstrate the new features of the theory with minimum complication, we neglect elasticity. Following Balluffi [16], we also neglect strains due to the space occupied by point defects such as vacancies or free volumes; enough dislocations climb or other defects move to maintain the point defects close to equilibrium concentrations, which are typically small. Consequently, a fixed volume contains a constant number of atoms at all time. The volume per atom, Ω, is constant. The net atomic flux is divergence-free, $N_{k,k}=0$, so that

$$v_{k,k} = -\Omega J_{k,k}. \tag{2}$$

A repeated subscript implies summation over 1, 2, and 3; a comma before a subscript indicates partial differentiation. Equation (2) has a clear interpretation. Imagine a volume fixed in space. When $J_{k,k}>0$, atoms diffuse out the volume; for the volume to maintain a constant number of atoms, convection must carry atoms into the volume, so that the markers converge. The opposite is true when $J_{k,k}<0$. In this theory, the material is incompressible, but the marker velocity has a divergence to compensate for the divergence in the diffusion flux. It is this kinematic constraint, Eq. (2), that couples creep and self-diffusion.

Markers at different locations may move at different velocities. When two markers move away from each other, atoms have to be inserted in the space between them. When two markers move toward each other, atoms have to be removed from the space between them. The gradient of the marker velocity field defines the strain-rate tensor:

$$d_{ij} = \tfrac{1}{2}(v_{i,j} + v_{j,i}). \tag{3}$$

If m_i is the unit vector pointing from one marker to the other, then $m_i d_{ij} m_j/\Omega$ is the number of atoms inserted or removed per unit time, per unit area normal to and per unit distance along the direction m_i. The strain rate is the sum of that due to diffusion, d_{ij}^D, and that due to creep, d_{ij}^C:

$$d_{ij} = d_{ij}^C + d_{ij}^D. \tag{4}$$

As suggested by Eq. (2), the divergence in the diffusion flux, $J_{k,k}$, causes the divergence in the marker velocity. We assume that the divergence in the diffusion flux causes an equal strain rate in all three directions:

$$d_{ij}^D = -\frac{\Omega}{3} J_{k,k}\delta_{ij}, \tag{5}$$

where $\delta_{ij}=1$ when $i=j$, and $\delta_{ij}=0$ when $i\neq j$.

A combination of Eqs. (2)–(5) gives the creep strain rates in terms of the marker velocity field:

$$d_{ij}^C = \tfrac{1}{2}(v_{i,j} + v_{j,i}) - \tfrac{1}{3} v_{k,k}\delta_{ij}. \tag{6}$$

The creep strain-rate tensor is symmetric and traceless.

3 Energetics

Figure 2 illustrates three types of load on the material. We identify them by the ways they supply power to the material. The wind force F_i supplies power $\int F_i J_i dV$, with the integral over the volume of the material. The traction t_i supplies power $\int t_i v_i dS$, with the integral over the material surface where the traction is prescribed. The chemical potential μ is the free energy difference between an atom on the material surface and an atom in a reference body (a bulk under no stress). The chemical potential is a scalar field defined on the material surface, in the same spirit as the traction is a vector field defined on the surface. We assume local equilibrium: The chemical potential of atoms in the material immediately beneath the surface equals that of atoms on the surface. Let the unit vector n_i be normal to the surface and point to the outside of the material, and $J_i n_i$ be the flux at which the atoms diffuse out the material. The chemical potential acts on atoms in the same way as the voltage acts on electrons. When atoms diffuse out of the material and join the reference body (i.e., when atoms move across the chemical potential), the chemical potential supplies power $-\int \mu J_i n_i dS$, with the integral over the material surface where the chemical potential is prescribed.

We next identify driving forces for the two rate processes, following an approach often used in constructing continuum theories of multiple rate processes and thermodynamic forces, e.g., [17]. We state the principle of virtual power in the form of the balance between power dissipation and power supply:

$$\int (s_{ij}d_{ij}^C + f_i J_i)dV + \int \lambda(v_{k,k} + \Omega J_{k,k})dV = \int F_i J_i dV + \int t_i v_i dS - \int \mu J_i n_i dS. \tag{7}$$

On the right-hand side of Eq. (7) are the three modes of power supply discussed above. On the left-hand side, the first integral contains two modes of power dissipation. Equation (7) defines the creep driving force, s_{ij}, as the power-conjugate of the creep strain rate. Because d_{ij}^C is a symmetric and traceless tensor, without loss of generality, we require that s_{ij} be a symmetric and traceless tensor. Eq. (7) defines the diffusion driving force, f_i, as the power-conjugate of the diffusion flux. The second integral enforces the kinematic constraint, Eq. (2), with λ as the Lagrange multiplier.

Because s_{ij} is a symmetric and traceless tensor, and d_{ij}^C relates to the marker velocity field by Eq. (6), we confirm that $s_{ij}d_{ij}^C = s_{ij}v_{i,j}$. Using the divergence theorem, we can express Eq. (7) as

$$-\int (s_{ij} + \lambda\delta_{ij})_{,j} v_i dV + \int ((s_{ij} + \lambda\delta_{ij})n_j - t_i)v_i dS + \int (f_i - F_i - \Omega\lambda_{,i})J_i dV + \int (\Omega\lambda + \mu)J_i n_i dS = 0. \tag{8}$$

This equation holds for arbitrary marker velocity and diffusion flux field, with no constraint. Consequently, the power balance requires that

$$(s_{ij} + \lambda\delta_{ij})_{,j} = 0, \quad \text{in volume} \tag{9}$$

$$(s_{ij} + \lambda\delta_{ij})n_j = t_i, \quad \text{on surface} \tag{10}$$

$$f_i = F_i + \Omega\lambda_{,i}, \quad \text{in volume} \tag{11}$$

$$\mu = -\Omega\lambda, \quad \text{on surface.} \tag{12}$$

Equation (9) and (10) recover force balance equations. In familiar terms, the creep driving force s_{ij} is the deviatoric stress tensor, the Lagrange multiplier λ is the mean stress σ, and the combination $\sigma_{ij} = s_{ij} + \sigma\delta_{ij}$ is the Cauchy stress tensor. Equations (11) and (12) recover Herring's equations for the diffusion driving force, [4,8]. The quantity $-\Omega\sigma$ is the free energy change associated with transferring an atom in the stress-free reference body to a point inside the material under the mean stress σ. In short, $-\Omega\sigma$ is the chemical potential inside the material. Its gradient, together with the wind force F_i, drives diffusion. To maintain local equilibrium, the chemical potential in the material just beneath the surface matches the prescribed value on the surface.

Following the established usage in mechanics, we intend the phrase "virtual power" to mean that Eq. (7) holds true provided all the kinematic relations are satisfied, and that no constitutive relations are assumed between the kinematic quantities and the force-like quantities. We could have as well followed an equivalent approach by invoking stress potential and strain rate potential, [18]. This paper considers isothermal phenomena. Were we interested in phenomena with nonuniform temperature fields, we would follow the practice of the nonequilibrium thermodynamics, working with the entropy production, [19].

4 Kinetics

Familiar isotropic kinetic laws are prescribed for diffusion and creep. The diffusion flux is proportional to the diffusion driving force:

$$J_i = \frac{Df_i}{\Omega kT}, \tag{13}$$

where D is the self-diffusion coefficient, k Boltzmann's constant, and T the temperature. The creep strain rate relates to the deviatoric stresses as

$$d_{ij}^C = \frac{s_{ij}}{2\eta}, \tag{14}$$

where η is the viscosity. For linear creep, η is constant. For nonlinear creep, a standard approach is to assume that η is a function of either the effective stress $\sigma_e = (3s_{ij}s_{ij}/2)^{1/2}$, or the effective creep strain rate $d_e^C = (2d_{ij}^C d_{ij}^C/3)^{1/2}$. The function $\eta(\sigma_e)$ or $\eta(d_e^C)$ is determined by fitting to the relation between stress and strain rate measured under a simple stress state.

5 Governing Equations and Characteristic Length

Inserting the creep law (14) and creep strain-rate expression (6) into the force balance Eq. (9), we obtain that

$$[\eta(v_{i,j} + v_{j,i} - \tfrac{2}{3}v_{k,k}\delta_{ij})]_{,j} + \sigma_{,i} = 0. \tag{15}$$

Inserting the diffusion law (13) and diffusion driving force expression (11) into the kinematic constraint (2), we obtain

$$v_{k,k} = -\left[\frac{D}{kT}(F_k + \Omega\sigma_{,k})\right]_{,k}. \tag{16}$$

When the diffusion flux divergence vanishes, the marker velocity divergence also vanishes, $v_{k,k} = 0$; Eq. (15) reduces to Stokes's equation for creep, and Eq. (16) reduces to Herring's equation for self-diffusion. In general, $v_{k,k} \neq 0$, and Eqs. (15) and (16) are four coupled partial differential equations that govern the marker velocity v_i and the mean stress σ. Each point on the material surface requires four boundary conditions: three conditions of either velocities or tractions, one condition of either chemical potential or the diffusion flux component normal to the surface.

The theory has a characteristic length. When D and η are constant, Eqs. (15) and (16) are linear. Let σ_0 be a representative stress scale in a boundary problem, and Λ be the length scale to be determined. Scale the stresses by σ_0, the velocities by $\Lambda\sigma_0/\eta$, the wind forces by $\Omega\sigma_0/\Lambda$, and the spatial coordinates by Λ. Equations (15) and (16) become dimensionless and parameter-free provided

$$\Lambda = \sqrt{D\eta\Omega/kT}. \tag{17}$$

The length characterizes the relative rate of diffusion and creep, and is independent of the scale of the stress.

For polycrystals, when creep is facilitated by diffusion, either through grains or along grain boundaries, the viscosity scales with the grain size d_g as $\eta = kTd_g^2/42D\Omega$, [20], so that the characteristic length scales with the grain size, $\Lambda = d_g/\sqrt{42}$. For simple liquids, the self-diffusivity is estimated by the Stokes-Einstein formula, [12], $D = kT/6\pi a\eta$, where a is atomic radius, so that the characteristic length scales with the atomic size, $\Lambda = \sqrt{\Omega/6\pi a}$. It is important to determine this length for more complex materials, such as amorphous metals and polymer melts.

If the creep data under the uniaxial tensile stress state fit the power law, $d_{11}^C = B\sigma_{11}^n$, where B and n are constants, the function η is given by

$$\eta(\sigma_e) = \frac{1}{3B\sigma_e^{n-1}}, \quad \text{or} \quad \eta(d_e^C) = \frac{1}{3B^{1/n}(d_e^C)^{1-1/n}}. \tag{18}$$

For power-law creep, with a constant diffusivity D, the solution to Eqs. (15) and (16) has a remarkable scaling structure. Let σ_* be a representative stress scale in a boundary problem, $d_*^C = B\sigma_*^n$, $\eta_* = \eta(\sigma_*)$, and Λ_* be a length scale. Scale the stress field by σ_*, the strain-rate field by d_*^C, the velocity field by $d_*^C\Lambda_*$, the

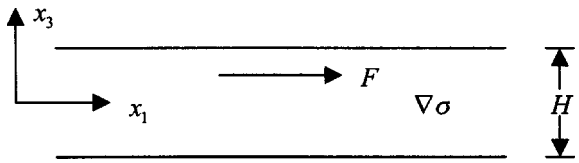

Fig. 3 A conductor film, sandwiched between dielectrics, is subject to an electron wind force and a stress gradient. The stress gradient can cause both a self-diffusion flux and a creep flow.

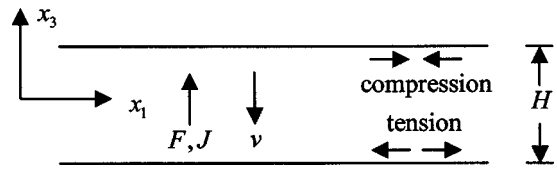

Fig. 4 A thin conductor subject to a through-thickness wind force. The diffision flux is in the same direction as the wind force, and the marker velocity is in the opposite direction. Tension is generated near one face of the film, and compression the other.

wind force field by $\Omega\sigma_*/\Lambda_*$, and the spatial coordinates by Λ_*. In terms of the dimensionless fields, the governing Eqs. (15)–(17) have only one parameter, the power index n, provided we identify the length Λ_* with Eq. (17), and replace η with η_* in the expression. For a power-law creep material, the length depends on the stress level σ_*. For polycrystals this length relates to a length L identified by Needleman and Rice [15], $\Lambda_*=\sqrt{L^3/3d_g}$. These authors also tabulated the experimental data for the length L for several metals.

6 Examples

6.1 Flow in a Film Driven by Stress Gradient and Electron Wind. In an interconnect line encapsulated in a dielectric, when the electron wind drives atoms to diffuse toward the anode, compression develops near the anode, and tension develops near the cathode. The stress gradient drives atoms to flow toward the cathode, in the direction opposite to the electron wind. It was discovered that the stress gradient could counter the electron wind, so that net mass flow vanished, [4]. This discovery has since become an effective means to avert electromigration failure; see recent reviews, [21,22]. In their original paper [4], Blech and Herring asserted that mass flow stops when the driving force for diffusion vanishes, namely, $F+\Omega\nabla\sigma=0$, where F is the electron wind force, and $\nabla\sigma$ the stress gradient. This assertion neglects a daily experience: The stress gradient also drives creep flow in a channel (e.g., in pumping water through a pipe). Given that the stress gradient can drive both a creep flow and a diffusion flow, will creep flow be also significant enough to counter electromigration?

To answer this question, consider a conductor film, thickness H, sandwiched between two dielectrics (Fig. 3). Let the axis x_3 be normal to the film, and the two faces of the film coincide with the planes $x_3=\pm H/2$. We will first analyze a steady flow subject to a constant electron wind force F and a constant stress gradient $\nabla\sigma$. For simplicity, we assume that both diffusivity and viscosity are constant.

In the steady flow, the only nonzero component of the marker velocity is in the flux direction, and varies in the thickness direction; that is, $v_2=v_3=0$ and $v_1=v_1(x_3)$. Consequently, the velocity field has no divergence, and convection and diffusion decouple. Of the pair of the governing equations, Eq. (16) is satisfied automatically, and Eq. (15) reduces to $\eta\partial^2 v_1/\partial x_3^2+\nabla\sigma=0$. This is an ordinary differential equation for the velocity profile $v_1(x_3)$. The gradient in the hydrostatic stress can induce a shear stress. Assuming the no-slip boundary condition at the conductor/dielectric interface, we obtain the familiar parabolic velocity profile: $v_1=((H/2)^2-x_3^2)\nabla\sigma/2\eta$.

The flow in the film has two contributions: the creep flow $Q^C=\int_{-H/2}^{+H/2}v_1dx_3=H^3\nabla\sigma/12\eta$, and the diffusion flow $Q^D=HJ_1=H(D/\Omega kT)(F+\Omega\nabla\sigma)$. First consider flow under the stress gradient alone, in the absence of the wind force F. The ratio of creep flow to diffusion flow is

$$Q^C/Q^D=H^2/12\Lambda^2, \tag{19}$$

where Λ is the length defined by Eq. (17). For a flow driven by the stress gradient, creep dominates in thick films, and diffusion dominates in thin films. Recall that Λ scales with the grain size for polycrystals, and with the atomic size for liquids.

In the presence of both the wind force and the stress gradient, the combined flow due to creep and diffusion vanishes when

$$F+\left(1+\frac{H^2}{12\Lambda^2}\right)\Omega\nabla\sigma=0. \tag{20}$$

The contribution of creep in countering electromigration depends on the film thickness. This effect is small in the exiting technology. To enhance the creep effect, we have to accelerate creep relative to diffusion, so that the length Λ becomes much smaller than the film thickness. For example, Λ approaches the atomic dimension for a liquid metal. The effect of creep can probably be demonstrated in laboratories, but there is no clear way to implement the effect in the electronic industry. Such an implementation would call for a material with both a large creep rate and a high electric conductivity.

6.2 Stress Generated by Electromigration Through Film Thickness. Figure 4 illustrates a metal film sandwiched between two other conductors, with electric current through the film thickness. The two outside conductors do not suffer electromigration, but the film does. This setup idealizes a contact. The electron wind force, F, now in the x_3-direction, causes atoms of the film to diffuse from one side to the other. Consequently, a state of stress is generated, tensile on one side and compressive on the other. The stress state is biaxial, $\sigma_{11}=\sigma_{22}$; all other stress components vanish. The mean stress component is $\sigma=2\sigma_{11}/3$. The stress is the function of the depth, $\sigma_{11}(x_3)$, and is to be determined.

The diffusion flux is a long the x_3-direction, given by

$$J_3=\frac{D}{\Omega kT}\left(F+\frac{2\Omega}{3}\frac{\partial\sigma_{11}}{\partial x_3}\right). \tag{21}$$

Because the net atomic flux vanishes, the markers move in the direction opposite to the diffusion flux, $v_3=-\Omega J_3$. The diffusion flux induces a strain rate $d_{11}^D=-(\Omega/3)\partial J_3/\partial x_3$. The deviatoric stress component is $s_{11}=\sigma_{11}/3$. The creep strain rate is proportional to the deviatoric stress, $d_{11}^C=\sigma_{11}/6\eta$. The film is constrained by the refractory metals, so that the strain rates vanish in the two lateral directions: $d_{11}=d_{22}=0$. The strain rate is the sum of that due to diffusion, and that due to creep. The sum vanishes:

$$-\frac{2D\Omega}{9kT}\frac{\partial^2\sigma_{11}}{\partial x_3^2}+\frac{\sigma_{11}}{6\eta}=0. \tag{22}$$

This is a second-order differential equation for $\sigma_{11}(x_3)$.

Atoms do not diffuse in or out the refractory conductors, so that the diffusion flux vanishes at the two faces of the film. Subject to these the boundary conditions, the solution to the differential equation is

$$\sigma_{11}(x_3)=-\frac{3Fl\sinh(x_3/l)}{2\Omega\cosh(H/2l)}. \tag{23}$$

The characteristic length is $l=\sqrt{4D\eta\Omega/3kT}$, which differs from the length identified in Section 5 by a numerical factor. The stress

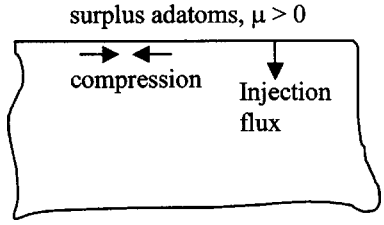

Fig. 5 An excess of the chemical potential on the surface drives atoms to inject into the material, leading to compressive stress

vanishes at the middle of the film, tensile on one side, and compressive on the other. When the diffusivity or viscosity is large, electromigration is rapid, and the material creeps slowly, so that the magnitude of the stress is large.

6.3 The Effect of Elasticity. When the electric current just starts, atoms have yet migrated much, and the stress in the film is negligible. This time-dependence is absent in the above solution. The problem arises because we have neglected elasticity. In this case, the geometric change is small, and we can include elasticity easily. The biaxial stress causes an elastic strain rate $d_{11}^E=[(1-\nu)/E]\partial\sigma_{11}/\partial t$. The combined strain rate due to diffusion, creep and elasticity vanishes:

$$-\frac{2D\Omega}{9kT}\frac{\partial^2\sigma_{11}}{\partial x_3^2}+\frac{\sigma_{11}}{6\eta}+\frac{1-\nu}{E}\frac{\partial\sigma_{11}}{\partial t}=0. \tag{24}$$

The problem now has a time scale $\tau=6(1-\nu)\eta/E$. The stress no longer changes instantaneously, but builds up gradually. The stress distribution given by (23) is the steady state, reached over the time scale τ.

6.4 Stress Generated by Atomic Injection or Emission The chemicalpotential μ on the surface can be varied in several ways, by applying a stress normal to the surface, by creating excess number of adatoms with an impinging flux, or by creating excess number of vacancies by oxidation. A surplus or deficit in the chemical potential will motivate atoms to diffuse in or out the material, leading to biaxial compression or tension (Fig. 5). Let the bulk of the material occupies the half-space $x_3<0$. The stress is prescribed by the chemical potential, $\sigma_{11}=\sigma_{22}=-3\mu/2\Omega$, on the surface, and vanishes as $x_3\to-\infty$. Equation (22) governs the stress as a function of the depth, giving

$$\sigma_{11}(x_3)=-\frac{3\mu}{2\Omega}\exp(x_3/l). \tag{25}$$

The chemical potential of the surface atoms sets the magnitude of the stress field. The stress decays exponentially over the length l.

6.5 Lateral Expansion or Contraction of a Free-Standing Film. Next consider a free-standing thin film. When the film thickness is on the order of the length l, the lateral constraint is partially relieved, and the film will expand or contract. The lateral strain rate d_{11} is independent of position x_3. The strain rate is the sum of that due to diffusion, and that due to creep:

$$d_{11}=-\frac{2D\Omega}{9kT}\frac{\partial^2\sigma_{11}}{\partial x_3^2}+\frac{\sigma_{11}}{6\eta}. \tag{26}$$

Force balance requires that the resultant force vanish: $\int_{-H}^{+H}\sigma_{11}(x_3)dx_3=0$. The solution to the ordinary differential equation is

$$\sigma_{11}(x_3)=\left(-\frac{3\mu}{2\Omega}\right)\frac{(H/2l)\cosh(x_3/l)-\sinh(H/2l)}{(H/2l)\cosh(H/2l)-\sinh(H/2l)}. \tag{27}$$

The lateral strain rate is

$$d_{11}=\left(\frac{\mu}{4\eta\Omega}\right)\frac{\sinh(H/2l)}{(H/2l)\cosh(H/2l)-\sinh(H/2l)}. \tag{28}$$

If atoms emit or inject preferentially at one of the film surfaces, the film will bend. The above analysis can be extended to calculate the rate at which the bending curvature increases.

6.6 Effect of Nonlinear Creep. Again consider the stress generated in a semi-infinite material by atomic injection or emission at the surface. Under the biaxial stress state, $\sigma_{11}=\sigma_{22}$, the equivalent stress is $\sigma_e=|\sigma_{11}|$. The lateral creep strain rate is $d_{11}^C=B/2\,|\sigma_{11}|^{n-1}\sigma_{11}$. The combined strain rate due to diffusion and creep vanishes:

$$-\frac{2D\Omega}{9kT}\frac{\partial^2\sigma_{11}}{\partial x_3^2}+\frac{B}{2}|\sigma_{11}|^{n-1}\sigma_{11}=0. \tag{29}$$

The solution of the boundary value problem is

$$\sigma_{11}(x_3)=-\frac{3\mu}{2\Omega}\left(1-\frac{x_3}{l_*}\right)^{-2/(n-1)}, \tag{30}$$

with

$$l_*=\frac{2}{n-1}\sqrt{\frac{2(n+1)\Omega D}{9|3\mu/2\Omega|^{n-1}BkT}}. \tag{31}$$

This length differs from the length identified in Section 5 by a numerical factor. Compared to the linear creep, the power-law creep modifies both the decay length and the decay function. For a large value of n the stress is substantial over a depth several times l_*.

7 Anisotropic Placement Rule

Equation (5) has been called the isotropic placement rule, [11]. We caution that this rule must be modified if atoms can be removed and inserted preferentially on some planes. For example, Fig. 6 illustrates a polycrystalline aluminum film, of columnar grain structure in the direction of the film thickness, and the native oxide covering the film surfaces. Aluminum diffusion is fast along the grain boundaries, and negligible on the film surfaces. Consequently the divergence in the self-diffusion flux will place atoms. We now extend the theory on the basis of an anisotropic placement rule.

Recall that, according to Eq. (2), the divergence in the diffusion flux causes the divergence of the marker velocity field. The issue is how to proportion this divergence in various directions. Our anisotropic placement rule stipulates that

$$d_{ij}^D=-\beta_{ij}\Omega J_{k,k}. \tag{32}$$

Here the coefficients β_{ij} weigh the placement in different directions. We require the tensor β_{ij} to be symmetric with a unit trace, $\beta_{ii}=1$. Consistent with this placement rule, the creep strain-rate tensor relates to the marker velocity field as

$$d_{ij}^C=\tfrac{1}{2}(v_{i,j}+v_{j,i})-\beta_{ij}v_{k,k}. \tag{33}$$

The creep strain-rate tensor is symmetric and traceless.

The statement of power balance still takes the form of Eq. (7). However, the creep dissipation rate now becomes $s_{ij}d_{ij}^C=s_{ij}v_{i,j}-\beta_{ij}s_{ij}v_{k,k}$. This will modify Eq. (8) by replacing $s_{ij}+\lambda\delta_{ij}$ in the two places by $s_{ij}+(\lambda-\beta_{pq}s_{pq})\delta_{ij}$; the rest of Eq. (8) remains unchanged. We now identify $(\lambda-\beta_{pq}s_{pq})$ as the mean stress σ, so that $\lambda=\sigma+\beta_{pq}s_{pq}=\beta_{pq}\sigma_{pq}$. It is the chemical potential $-\Omega\beta_{pq}\sigma_{pq}$ that enters Herring's equations of diffusion driving force, Eqs. (11) and (12). We may also wish to introduce anisotropy into the kinetic laws, Eqs. (13) and (14), which we will not pursue here.

As an example, when diffusion flux divergence is placed equally in the x_1 and x_2-directions, but not in x_3-direction, we let $\beta_{11}=\beta_{22}=1/2$, and all other components vanish. Consequently,

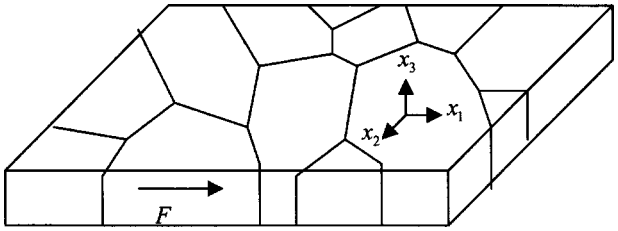

Fig. 6 An aluminum film has a columnar grain structure, with top and bottom surfaces covered by the native oxide. Under an electron wind force in the plane of the film, aluminum atoms diffuse fast on the grain boundaries, but negligibly on the film surfaces. The divergence of the diffusion flux will place atoms in the x_1 and x_2-directions, but not in the x_3-direction.

the chemical potential in the material becomes $-\Omega(\sigma_{11}+\sigma_{22})/2$. The work is done by the stresses acting in the direction where mass insertion or removal occurs.

8 Summary

Both convection and diffusion contribute to mass transport. Identify convection by the motion of markers dispersed in the material. Creep and self-diffusion couple because the markers must move to compensate for the diffusion flux divergence, Eq. (2). We stipulate rules to place the diffusion flux divergence to various planes; two versions are given: isotropic rule Eq. (5) and anisotropic rule Eq. (33). We define the driving force for creep and diffusion by a statement of power balance, Eq. (7), subject to the kinematic constraint. The theory leads to partial differential equations for the marker velocity field and the chemical potential field, Eqs. (15) and (16). The pair of equations generalizes Stokes's creep and Herring's diffusion. A length characterizes the relative rate of diffusion and creep, Eq. (17). Several boundary value problems illustrate the theory. In particular, a stress gradient can drive both a diffusion flow and a creep flow. Diffusion flow prevails in a thin channel, and creep flow prevails in a thick channel. The transition occurs when the channel thickness is comparable to the characteristic length of the material.

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